SPECTROSCOPIC STUDIES OF COAL PYRIDINE EXTRACTS

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This study is part of a larger program aimed at developing an FTIR methodology for the quantitative determination of the aliphatic and aromatic CH content of coals. Although a number of infrared studies of these quantities have appeared, there remains significant differences in the values reported by different groups, reviewed in reference 1. A recent publication by Solomon and Carangelo (2) is not included in this review and is a significant addition to the literature. The origin of these discrepancies is largely due to the difficulty in determining adsorptivities or absorption coefficients, those quantities that relate the intensity of an infrared band to the concentration of functional groups giving rise to that particular absorption. There are essentially three ways of doing this:

a) calibrate using model compounds;
b) equate the hydrogen content (from elemental analysis) to the sum of the functional group contributions;
c) calibrate using soluble coal extracts.

The first is obviously unsatisfactory, not least because it begs the question "what is the structure of coal and hence what is an appropriate model compound." The second method was pioneered, in its application to FTIR studies, by Peter Solomon and his group (2-5), but is equivalent to a procedure described by von Tschamler and deRuiter more than 25 years ago (6). The hydrogen content of the coal is equated to the sum of the contributions from various functional groups

$$H_T = H_{OH} + H_{ar} + H_{al}$$

where the total hydrogen content H_T is measured by elemental analysis and H_{OH} is determined by FTIR or other measurements. [COOH groups should also be measured in low rank coals]. Then;

$$[H_T - H_{OH}] = E_{ar}I_{ar} + E_{al}I_{al}$$

where E_{ar} and E_{al} are "conversion factors" (an inverse function of the absorption coefficients) and I_{ar} and I_{al} are the intensities of appropriate infrared bands. If a set of coals of roughly the same character (rank) are studied, we can assume E_{ar} and E_{al} are constants for that set and, from the experimentally measured values of H_T, h_{OH}, I_{ar} and I_{al}, solve as a set of simultaneous equations for E_{ar} and E_{al}. As we have found in previous studies, however, this set of simultaneous equations is classically ill-conditioned (reviewed in detail in reference 1). In other words, even small experimental errors in a limited sample set results in the calculation of a range of almost equally valid solutions. In their recent study Solomon and Carangelo (2) employ the same method, seeking to improve the accuracy of their calculations by including data from coal chars, and conclude that there is also a variation in absorption coefficients with rank. They are no doubt right, but the problems with this methodology have not been overcome. Furthermore, in forming chars certain types of alkyl groups are preferentially cleaved and lost as volatiles while the remainder of the coal molecule undergoes a degree of reorganization that depends upon the conditions of char formation. This could also lead to some variation in absorption coefficients.

The final method listed relies on the fact that the aromatic and aliphatic CH content of soluble material can be directly determined by proton nmr, thus allowing the absorption coefficients of infrared

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bands of the same sample to be unambiguously calibrated. Of course, if the extract is significantly different in structure to the parent coal, thus having different absorption coefficients, these values would not be transferable. This is indeed the case for those coals where there is a high proportion of extractable long chain alkanes. Fortunately, the CH stretching vibrations of paraffin-like materials are characteristically sharp and readily recognizable and the correspondence in the spectra of most extracts and their parent coals demonstrates a similarity in structure. Clearly, in order to determine the range of absorption coefficients associated with coal structure of varying degrees of aliphatic character by this method it is necessary that we obtain and study a wide range of samples. This serves to define the range of inevitable experimental error.

Accordingly, at this point we see no substitute for a slow, meticulous, brute-force approach to data collection and analysis. During the past 3 years we have obtained the pyridine extracts of more than thirty-five U.S. coals and seventeen Polish coals. In this brief communication space does not permit a full description of the characteristics of these samples and the details of our analytical procedures; these will be presented elsewhere, but the FTIR methodology is similar to that described previously (1). Here we will simply present an overview of our results.

The data from proton nmr studies of the coal extracts, together with elemental analysis and a knowledge of the OH content (from FTIR studies of acetylated samples), allows the aromatic and aliphatic hydrogen contents of the coals to be determined. Preliminary results are shown in figure 1. Although there is some scatter, to be expected from materials as heterogeneous as coal, the data is fairly closely grouped and clearly shows the expected trend of decreasing aliphatic CH content and increasing aromatic CH content with rank (% carbon content of parent coal).

In principle, this data can now be applied to a determination of the absorption coefficients of infrared bands assigned to aromatic and aliphatic CH groups. In practice, errors play a major role in determining the accuracy of this procedure. Figure 2 shows a plot of the ratio of the intensities of the aromatic and aliphatic CH stretching modes, determined as band areas (from samples prepared as KBr pellets) by curve-resolving procedures described elsewhere (1). There is some scatter in the results that is not simply a matter of the natural variability of aromatic and aliphatic CH content in coals from different sources. Obviously, a plot of the ratio of the intensities of the infrared bands should follow the ratio determined by proton nmr. This relationship need not be linear, if absorption coefficients vary with rank, but should at least be systematic Figure 3 shows that although a consistent trend can be obtained and a reasonable average value of the ratio of absorptivities determined, the effect of cumulative errors in the data is such that it is not possible to determine any variation with rank with any degree of certainty. The precision in this data can only be improved by averaging the results of additional spectroscopic analysis of these samples, a time consuming process which we are presently in the process of performing.

Finally, we are also analyzing the same samples by diffuse reflectance measurements, so that the two FTIR methodologies can be directly compared. A plot of the ratio of intensities of the aromatic to aliphatic CH stretching modes against the ratio of the aromatic to aliphatic CH content determined by proton nmr is shown in Figure 4. The ratio of the values of the absorption coefficients is somewhat different to that determined from KBr pellets, but again errors, particularly in some of the high rank (larger H_{ar}/H_{al} ratio) coals necessitates additional work. Again a reasonable average value can be determined, but the subtleties of variation with rank are beyond detection given the present precision of the data.

Acknowledgment

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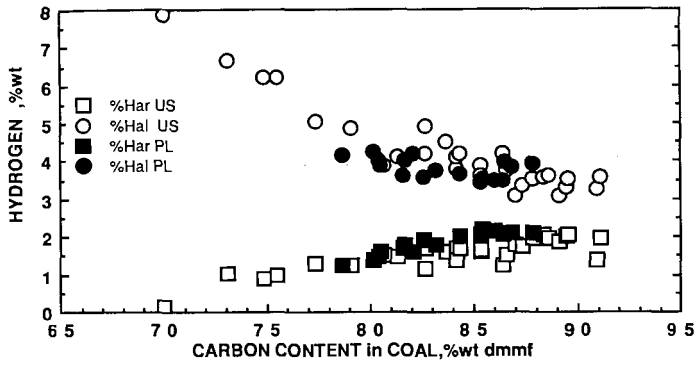

Figure 1. Plot of the aliphatic and aromatic hydrogen content of a set of U.S. and Polish (PL coals), determined by proton nmr.

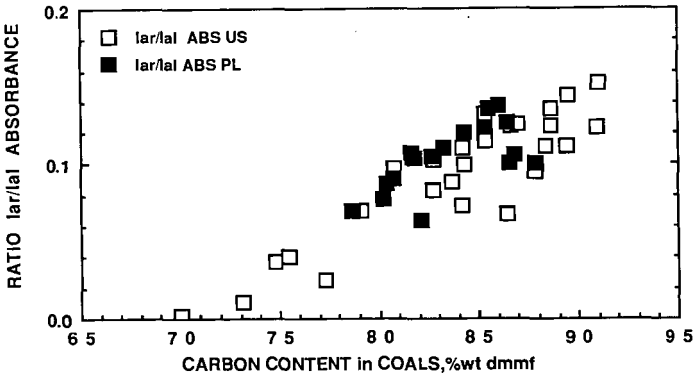

Figure 2. Plot of the ratio of the infrared band areas of the aromatic and aliphatic CH stretching modes for the set of extracts.

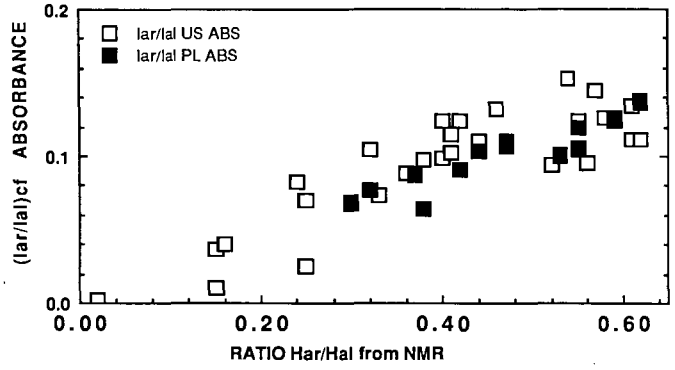

Figure 3. Plot of the ratio of the band areas of the aromatic and aliphatic infrared stretching modes vs the ratio H_{ar}/H_{al} determined by proton nmr.

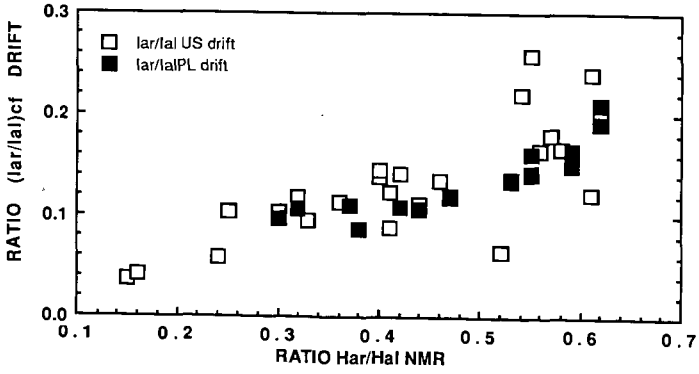

Figure 4. Plot of the ratio of the aliphatic to aromatic CH stretching modes determined by DRIFT to the ratio H_{ar}/H_{al} determined by proton nmr.

LASER ABLATION FOURIER TRANSFORM MASS SPECTROMETRIC INVESTIGATION OF COALS AND RELATED MODEL SUBSTANCES

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INTRODUCTION

Laser ablation Fourier transform mass spectrometry (LA/FTMS) is a technique which allows the investigation of high molecular weight involatile materials. Coals and cokes represent a class of such materials and in general, mass spectrometric analyses of such carbonaceous materials have generally been restricted to thermal desorption gas chromatography-mass spectrometry. Batts and Batts [1] have recently reviewed the application of mass spectrometry to coal analysis.

The use of pulsed high power lasers in mass spectrometry as a soft ionization technique is now well established and has facilitated the invest-igation of macromolecular species of several thousand mass units [2]. The pulsed nature of the Fourier transform mass spectrometer and high powered pulsed IR or UV lasers represents a logical combination for laser ablation experiments. This technique offers several advantages [2-4], the most important of which are high mass resolution and extended mass range, over other mass spectrometric methods which incorporate time-of-flight or deflection type analysers and other 'soft ionization' techniques.

The carbon content of coal directly reflects its rank and level of maturity. During coalification, the terrestrial organic matter is modified by geochemical processes to ultimately form anthracitic coals. Particularly significant is the transition observed at about 89% carbon content where aromatic lamellae in the coal begin to condense to form polycyclic aromatic compounds. These polynuclear species are important components of anthracitic coals where they form the basis for the further growth of graphite sheets.

In this study, we have examined by FTMS different rank coals and model systems. The latter include graphite and different ring size polynuclear aromatic hydrocarbons. The ionization mechanisms and the effects of irradiance conditions have also been examined.

EXPERIMENTAL

Table 1 presents the maceral compositions and elemental analyses data for the coal samples studied. These included two American anthracitic coals, obtained from the Pennsylvania State University sample bank, and an Australian semi-anthracitic coal and lignite. The graphite and individual polynuclear aromatic compounds were obtained from commercial sources, and were of such purity to be used as received.

The mass spectra were obtained using a Bruker CMS-47 FT/ICR mass spectrometer equipped with a 4.7T superconducting magnet and a 24 bit/256 kW Bruker ASPECT 3000 computer. The stainless steel high vacuum chamber and direct insertion probe were evacuated by Balsers 330 $lsec^{-1}$ and 50 $lsec^{-1}$ turbo molecular pumps, respectively. For the laser ablation experiments, the samples were finely powdered together with NaCl and pressed into a detachable cylindrical stainless steel satellite probe tip. This in turn was inserted, using a Bruker direct insertion probe, into a titanium single section cylindrical (r=30 mm, h=60 mm) ICR cell.

A typical laser ablation experiment involved focussing the laser beam (1064 nm, Spectra Physics DCR-11) of a Nd-YAG laser to 0.1 mm at the sample satellite probe tip. The sample surface was subjected to laser beam irradiances in the range of 0.005-1000 $MWcm^{-2}$, with reproducible irradiance variations being obtained by using neutral density filters. Two laser irradiance times were used in the experiments, corresponding to a long pulse mode (230 μs) and a Q-switched mode (8 nsec). Through careful regulation of the laser irradiance near the ionization threshold it was possible to monitor the effect of laser irradiance on the resulting mass spectra. A normal pulse sequence consisted of the laser irradiation followed by a 1 second delay, prior to data acquisition to allow the desorbed neutral species to be evacuated and the pressure to return to $1\text{-}10^{-8}$ mbar. Ions were trapped in the cell by potentials of approximately 4V. The transient was stored as 64 k data points prior to Fourier transformation to obtain a magnitude mode spectrum. For the results reported here, no attempt was made to improve resolution of the high mass carbon clusters by selecting smaller mass ranges, to improve the density of data points.

RESULTS AND DISCUSSION

Model Systems

Figure 1 shows the mass spectra of two of the polynuclear aromatic hydrocarbon compounds; chrysene and fluoranthene. The most abundant ions in each spectra result from the molecular ion, $M^{+\cdot}$ and the adduct ion $[M + X]^+$, where X is Na^+. This ion distribution was found for all the polynuclear aromatic model compounds, for the laser ablation experiments. This result indicates the occurrence of at least two different ionization pathways. The presence of adduct ions in the mass spectra indicates a surface laser desorption mechanism, with attachment of alkali metal ions to involatile molecules [5]. For example, in Figure 1(a) the adductlon of chrysene, $[C_{18}H_{12} + Na]^+$ (m/z 251) results from the attachment of Na^+ to the aromatic compound to form the ionized species, with subsequent volatilization by laser desorption.

In contrast, there is no information to allow a confident prediction of the $M^{+\cdot}$ molecular ion formation mechanism. It could be a laser desorption process, where simultaneous ionization and vaporization of the condensed phase leads to the formation of the $M^{+\cdot}$ ions. Alternatively, a multiphoton ionization mechanism where neutrals, which are desorbed by the initial part of the laser pulse, are ionised by photons in the latter part of the laser pulse may be occurring. Yet another possibility is ion/molecule reactions, where smaller desorbed species recombine in the emitted plasma cloud. However, the important point to note is that there is more than one ion formation mechanism possible [6] and it is unlikely in any high power laser ablation experiment that all ions are formed by a single ionization process. Considering the uncertainty concerning these ionization mechanisms for $M^{+\cdot}$ formation, it appears that laser desorption ionization of involatile surface species may only be unequivocally assigned from adduct ions.

Interestingly, laser ablation of the graphite sample (Figure 2(a)) at similar irradiation conditions as the model compounds gave only $M^{+\cdot}$ spectra. The mass distribution observed for the carbon cluster ions ranged from C_{11}^+ to C_{28}^+, with the most intense ions at C_{15}^+ and C_{19}^+. Laser ablation FTMS studies on graphite have been previously reported by McElvany *et al.* [7], who observed carbon clusters upto C_{180}^+, with the most stable species being C_{60}^+. Compared with the present study, this earlier investigation used (1) a different instrument configuration, (2) different irradiation conditions, and (3) ejected all species below C_{18}^+ to enhance the resolution of the higher molecular weight carbon clusters. It has also recently been reported that C_{60}^+ is remarkably stable and is, in fact, a spherical aromatic molecule with a truncated icosahedron (soccer ball) structure. Indeed, carbon clusters have been proposed as being important as nucleation agents for soot formation and being present in interstellar dust clouds [8].

The absence of $[M + Na]^+$ adduct ions in the mass spectrum means that it is difficult to determine, unequivocally, whether the carbon cluster ions are formed from surface species by simple volatilization and photodissociation (i.e. a laser desorption process) or are formed in the gas phase by the other ionization mechanisms, the latter of these being more likely [7]. It is also possible in laser desorption experiments that the adduct ions are not observed, as very large aromatic species may not necessarily form stable adducts with Na^+.

Negative ion carbon clusters have also been observed for the graphite sample (Figure 2(b)), with the largest cluster being at C_{25}^- (m/z 300). The detection of negative ions is easily performed in the FTMS by reversing the polarity of the trapping plate potentials. The negative ion carbon cluster distribution does not resemble that of the cations. Only smaller carbon cluster anions are stable. The difference between the anion and cation clusters can be attributed to a different mechanism of formation. The emitted plasma cloud is made up of ions, neutrals and electrons, and electron attachment is believed to be the mechanism of formation for the anionic clusters. It is reported that these carbon cluster anions do not undergo reaction with neutral carbon species in the plasma to form larger carbon clusters ($>C_{30}^-$) [7].

Coals

Laser ablation of all the anthracitic coals only generated charged carbon clusters. There was no evidence of adduct ion formation in the mass spectra, even when the samples were heavily doped (i.e. 20:1) with alkali metal salts. Figure 3(a&b) shows the mass distributions for the cationic (C_n^+ where $3<n<150$) and anionic (C_n^- where $2<n<25$) carbon clusters from the Australian anthracitic coal. The mass distributions are typical of those also observed for the two American anthracitic coals. In all cases, the most intense and stable cationic carbon cluster was C_{60}^+, and the mass distributions were similar to those previously reported for graphite [7].

It is also evident from figure 3(a) that the even numbered clusters have greatest stability, and Smalley et al. [9] have proposed a likely formation mechanism to account for this phenomenon. Formation of the high even mass carbon cluster cations has been attributed to ion/molecule reactions that occur in the laser desorbed plasma. Highly reactive carbon radicals ranging in size from one to twenty atoms are initially desorbed from the sample. These then react with each other to form the larger more stable even numbered clusters.

The mass distribution of the anionic carbon clusters (Figure 3(c)) is similar to that observed from the graphite sample. It would, therefore, appear the same mechanism as that proposed for graphite [7] also accounts for the low mass range distributions from the three anthracitic coals.

Another important factor which has been observed to influence the laser ablation mass spectra is the laser irradiance time. Figures 3(a&b) and (c&d) show the effect of different laser irradiance times (200 μs) and 8 ns) on the mass distributions of the cationic and anionic carbon clusters, respectively. It is believed that both the laser irradiance time and the molecular structure of the sample are important in determining the formation and mass distribution of the carbon clusters [7]. This is dramatically shown in the mass distributions of the cationic carbon clusters. The mass distribution produced at an irradiance time of 200 μs (Figure 3(d)) shows species up to C_{150}^+, while that produced with an irradiance time of 8 ns (Figure 3(b)) shows only a few lower mass range carbon clusters. In contrast, the mass distributions of the anionic carbon clusters (Figures 3(c&d)) show only a small variation with different irradiance times.

The mass distributions from the laser ablation experiments on the lignite (Figures 4 (a&b) are similar to those from the anthracitic coals. Again, the most intense and stable species in the mass distribution of the cationic carbon clusters, which range up to C_{150}^+, is C_{60}^+. Similarly, the mass distribution of

the anionic carbon clusters are, again also, below C_{25}^- . Apparently, the mechanisms which generate the cationic and anionic carbon clusters from the graphite and the anthracitic coals are the same as those forming ionic carbon clusters from the lignite.

The irradiation conditions used in our laser ablation experiments did not produce large (i.e. n > 30) carbon clusters from the graphite. However, no difficulty was encountered in generating these species from either the anthracitic coals or lignite. This observation suggests that more energy is required to break the highly ordered and strongly bonded covalent graphite lattice, than the structural components and linkages in coals.

CONCLUSIONS

1. A study of polynuclear aromatic hydrocarbons by FTMS has shown the viability of the technique for investigating surface species.
2. Cationic and anionic carbon clusters are generated from anthracitic coals and lignite.
3. Under the experimental conditions used in this investigation, the mass distributions of the cationic and anionic carbon clusters appear to be independent of coal rank, and similar to those previously reported for graphite.
4. The absence of $[M+Na]^+$ adducts in the mass distributions from the coals means that the carbon clusters cannot be unequivocally considered as being desorbed from the coal surface, but more likely are formed in the gas phase by alternate ionization mechanisms.
5. The formation and mass distributions of the cationic carbon clusters are dependent on the laser irradiation time.
6. The potential of FTMS for studying carbonaceous materials, such as coals and graphite, has been demonstrated. Further developments in the technique should provide greater insight into the structure and nature of these materials.

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TABLE 1 Geochemical data on coal samples

Sample[A] Identification	Seam	State/Country	Rank	Maceral Composition (%)			Elemental Composition (%)				
				Vitrinite	Inertinite	Exinite	C	H	N	O[B]	S
PSOC 628	Penna No.2	Pennsylvania/ USA	Anthracite	92	8	0	94.9[C]	3.4	1.0	0.1	0.6
PSOC 867	Primrose	Pennsylvania/ USA	Anthracite	78	22	0	96.9[C]	1.0	0.8	0.7	0.6
	Yarrabee	Queensland/ Australia	Semi-anthracite	41	59	0	90.5[D]	3.7	1.8	3.3	0.7
	Loy Yang	Victoria/ Australia	Lignite	95	2	3	69.2[D]	4.9	0.9	25.0	0.3

A - Pennsylvania State University sample bank; B - by difference; C - Analysis determined on a dry, mineral-matter-free basis; D - Analysis determined on a dry, ash-free basis

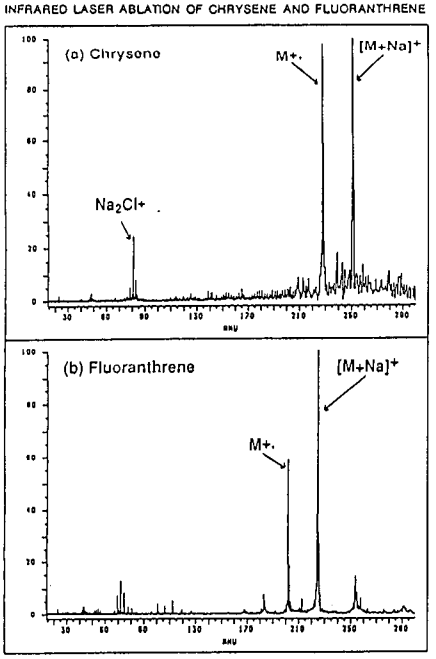

Fig. 1. Positive ion laser ablation FT-mass spectra of the model compounds (doped with 1:1 NaCl) (a) Chrysene and (b) Fluoranthane at 1600 MW/cm^2 with an irradience time of 8 ns.

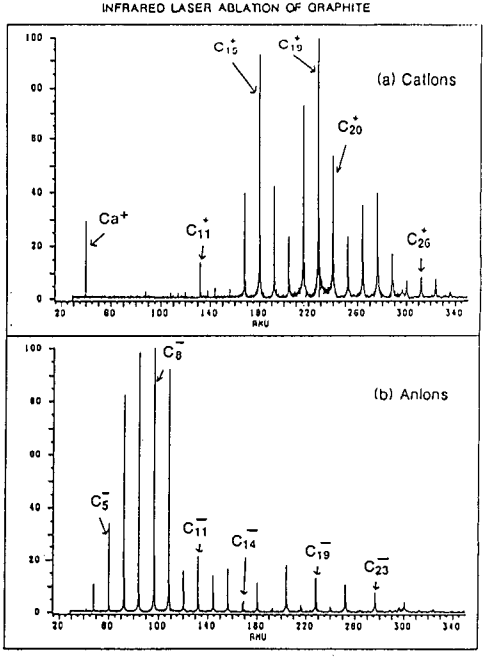

Fig. 2. (a) Positive and (b) negative ion laser ablation FT-mass spectra of graphite at 70 KW/cm^2 with an irradience time of 200 μs.

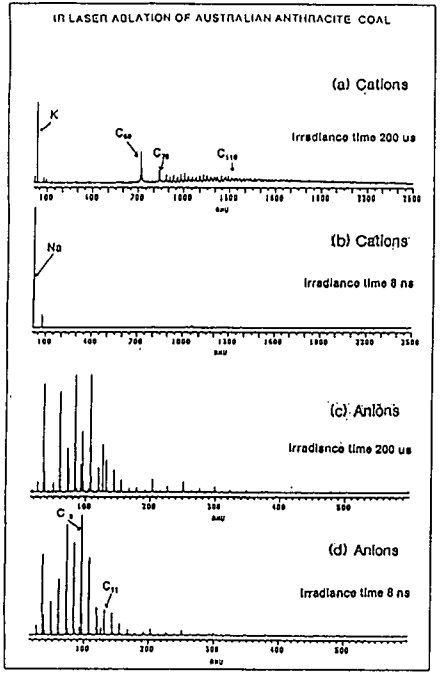

Fig. 3. (a-b) Positive and (c-d) negative ion laser ablation FT-mass spectra of an Australian anthracitic coal (doped with 1:1 NaCl) at 15 KW/cm^2, 10 MW/cm^2, 70 KW/cm^2 and 30 MW/cm^2 respectively.

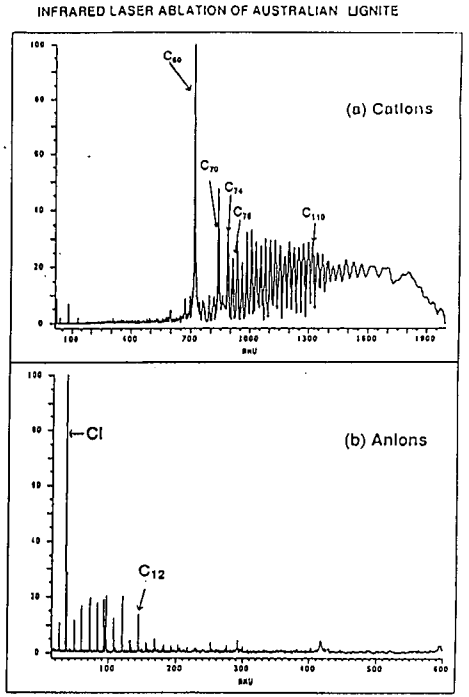

Fig. 4. (a) Positive and (b) negative ion laser ablation FT-mass spectra of an Australian lignite (doped with 1:1 NaCl) at 15 KW/cm^2 and 30 MW/cm^2 and an irradience time of 200 μs and 8 ns respectively.

MODELING OF COAL STRUCTURE USING COMPUTER-AIDED MOLECULAR DESIGN*

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Abstract

Knowledge of coal molecular structure is important in the understanding of coal reactivity. Computer-aided Molecular Design (CAMD) has been used to create and study 3-dimensional models of several postulated coal structures (Given, Wiser, Solomon, and Shinn). Using molecular dynamics calculations, a minimum-energy conformation for each structural model has been determined. Characteristics of the resulting coal structures will be discussed. Interactions of the structures with polar and non-polar solvent molecules are being explored to provide insight into coal pre-conversion chemistry. Future studies possible with this new tool will be outlined.

Introduction

The reactivity of coal is determined in substantial part by its chemical and physical structure. However, within any given coal there is considerable heterogeneity. Nonetheless, because of the strong link between structure and reactivity, there have been many attempts to model the macromolecular structure of various coals. For bituminous coals, the most widely accepted models developed during the past 30 years have been the aromatic/hydroaromatic structures, in which groups of about three aromatic rings, containing appropriate numbers and types of heteroatoms, are interconnected by hydroaromatic or aliphatic linkages (1-4). These models incorporate the average chemical and molecular characteristics of coal, and are not intended explicitly to represent actual "coal molecules". More recently, Spiro (5) has constructed physical space-filling models of several of these structures. Using the insight obtained from these models, he identified several steric difficulties in the original structures, and discussed the possible significance of the three-dimensional structures on mechanisms of coal pyrolysis.

Recently, computer-aided molecular design (CAMD) techniques have been developed to provide additional understanding of the structure and properties of complex molecular systems (6). Currently, CAMD techniques are being widely used in the pharmaceutical industry to guide the design and synthesis of a variety of biomolecules (drugs, enzymes, inhibitors, proteins). Using CAMD, one can not only construct a three-dimensional representation of a molecule, but can also convert the structure to an energy-minimized physical conformation, using molecular dynamics techniques. CAMD has been used to study basic coal structure (7), but not to examine the energetics of the structures. In this paper, CAMD is used to create three-dimensional models based on several postulated coal structures, and then to identify minimum-energy physical conformations for these models.

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Method

The CAMD studies described were carried out using BIOGRAF (BioDesign, Pasadena, CA), a software package for simulating organic and biological molecules. BIOGRAF allows the user to build molecules (structures), display them in a variety of formats (stick; dot surface; space-filling) and identify minimum energy conformations for them. The minimum energy conformations are found using molecular dynamics techniques with a suitable force-field approximation (6). In molecular dynamics, the energy of a structure is evaluated periodically as the atoms are allowed to move according to Newton's equations of motion at a specified "temperature" (which defines the atomic velocities). Dynamics runs usually involve many thousands of evaluation steps, representing the equivalent of many picoseconds of molecular motion. During the dynamics runs, structures twist and fold in ways which tend to optimize the non-bonded interactions (van der Waals, ionic, and hydrogen bonds), while maintaining appropriate bond lengths and angles.

BIOGRAF supports a number of force fields (AMBER, MM2, and DREIDING); in the current study, DREIDING was used. DREIDING is a very general force field that accounts for bond stretches and angles, torsions, and non-bonded interactions for a large number of atom types. Its accuracy is limited because it uses the same force constants for all atom types, although not for all types of interactions (i.e., the force constants for bond stretches are different from those for bending interactions, etc.). With this limitation, the energies calculated are most meaningful relative to one another, rather than in a quantitative sense. The BIOGRAF program was run on a MicroVAX II computer equipped with an Evans and Sutherland PS390 graphics terminal. The size of coal structures evaluated, and the duration of molecular dynamics runs, were limited by the available computing speed of this system (a 5000-step, 10-ps molecular dynamics run for a 1040-atom structure, with about 75,000 van der Waals interactions per step, required about 100 hours of computation).

Results

BIOGRAF was used to create three-dimensional models of four postulated bituminous coal structures, those of Given (1), Wiser (2), Solomon (3), and Shinn (4). After each of the models was created, it was converted into a minimum-energy physical conformation using molecular dynamics and energy minimization. Two of the structures, Given's and Shinn's, are shown in Figures 1 and 2. The Givens structure is shown because it has been widely cited as a possible representative coal structure. The Shinn structure represents the most complex coal structure in the literature, is also widely cited, and is similar in many ways to the Wiser and Solomon structures. Figures 1a and 2a show the two-dimensional molecular structures reported originally by Given and Shinn. These were used, with minor modifications, to create the computer space-filling models shown in Figures 1b and 2b (Given's structure was modified as suggested by Spiro (5) to eliminate a very strained quaternary carbon bond, and Shinn's structure was simplified by eliminating that fraction identified in his Table 5 as "residue", approximately 20% of the original structure). As the top and side views in Figure 2b show, the models are nominally two-dimensional at this point. Finally, Figures 1c and 2c show the minimum energy conformations adopted by the two models after 10-ps molecular dynamics runs. It is clear from the folding of these latter figures (especially Figure 2c) that simple two-dimensional representations probably do not adequately represent the coal structure. Significantly, the Given structure (Figure 1), constrained by pairs of methylene bridges between aromatic structures, is seen to be rather rigid. It did not change shape during molecular

dynamics as much as the Shinn structure, which folded up considerably due to van der Waals and hydrogen-bonding interactions. The Wiser and Solomon structures, not shown, behaved much like the Shinn structure during energy minimization.

To evaluate further the CAMD results, a program was written to extract a number of atomic and chemical parameters from each structure (number of atoms, fractions of aromatic carbon and hydrogen, weight fraction of each atomic species, empirical formula). The results were compared with the original literature for each structure. This provided a useful check on the accuracy of the computer models, which were rather complex (over 1000 atoms in the Shinn structure). In all cases, the CAMD models compared favorably with the literature values. Results of the computer analyses for the four structures analyzed are given in Table I. The total numbers of atoms only appear as guides to the size and complexity of each structure, and bear no relationship to the size of a "coal molecule" or a decomposition product. The most significant difference between the models appears to be in the values assumed for aromatic hydrogen. Given's value is much lower than those of the other authors and is probably incorrect, judging from more recent FTIR data (8). Given used pairs of methylene bridges extensively to satisfy his low ratio of aromatic hydrogen, thus explaining the major difference between his and the other structural models.

Also included in Table I is the minimum energy for each structure, calculated during molecular dynamics runs in which the "temperature" was reduced over a 10-ps period from 300 K to 10 K. In order to make the results more easily comparable, the energies are expressed per unit atom. The Given structure is energetically less favorable than the other three, because when it is considered as an isolated structure, its relative rigidity allows only minimal van der Waals and hydrogen-bond interactions. However, even if a number of Given structures were made to interact, their rigidity would still allow less non-bonded interactions, resulting in higher energy relative to the other structures. Thus, the Shinn, Wiser and Solomon structures appear at this time to be the more favored structures, based both on their more appropriate chemical characteristics and on their observed structural flexibility and energetic advantages.

Discussion

Three-dimensional models of postulated coal structures have been created, and minimum-energy conformations identified. For each of the three relatively flexible structures modeled, there was actually a large number of slightly different conformations with similar (low) energies. This suggests first that a number of nearly-equivalent structures might be equally probable in coal, and second, that structures with substantially lower energies than those identified are probably not likely. Although the ring structures in the energy-minimized Shinn structure (Figure 2c) show on the average no preferred orientation (although some local stacking was observed), the macrostructure is still somewhat anisotropic. If an extended structure based on the several units of the original quasi-planar Shinn structure had been constructed and energy-minimized, the anisotropy would have been more marked. This is in accord with Larson's experimental observations (9) that vitrinite samples have essentially randomly oriented organic groups (on a macroscopic scale), but at the same time show highly anisotropic mechanical and solvent swelling properties.

This work represents a first use of CAMD techniques to model coal structure and energetics. It has been possible to differentiate several postulated bituminous coal structures based on their three-dimensional character and their energetics. Obviously, these techniques could also be used to model coals of varying rank.

Modifications of the CAMD software are planned to allow the calculations of true and particle density of the coal structures. These density calculations will be especially important in the study of coal-solvent interactions, using both polar and non-polar solvents. Such studies should provide further insight into the nature of solvent swelling phenomena and the role of porosity in coal. Finally, although more difficult, it may be possible to model chemical interactions approximately using CAMD. In all, it appears that CAMD techniques represent a potentially very powerful new tool for studying the nature of coal structure and its effect on reactivity.

References

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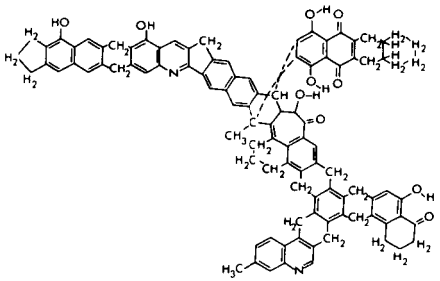
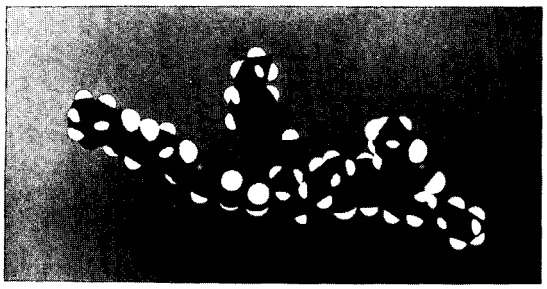
TABLE I

COAL STRUCTURAL PARAMETERS (Weight Fraction DMMF)

Parameter	Given	Wiser	Solomon	Shinn
# Atoms	193	390	326	1040
C_{Ar}	0.66	0.71	0.74	0.71
H_{Ar}	0.21	0.29	0.36	0.34
Wt. Fraction				
C	0.82	0.76	0.81	0.79
H	0.053	0.057	0.055	0.056
O	0.107	0.112	0.096	0.113
N	0.019	0.014	0.011	0.014
S	---	0.053	0.026	0.020
Energy/Atom (kcal/atom)	2.01	1.60	1.58	1.55
Formula (normalized)	$C_{100}H_{77}O_{9.8}N_{2.0}$	$C_{100}H_{89}O_{11}N_{1.6}S_{2.6}$	$C_{100}H_{82}O_{8.9}N_{1.2}S_{1.2}$	$C_{100}H_{85}O_{11}N_{1.5}S_{1.0}$



a)



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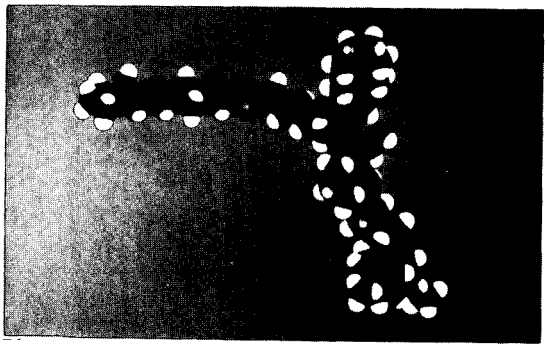

c)

Figure 1. Given structure. a) Structure from literature; b) Initial CAMD-generated structure; c) Energy-minimized CAMD structure.

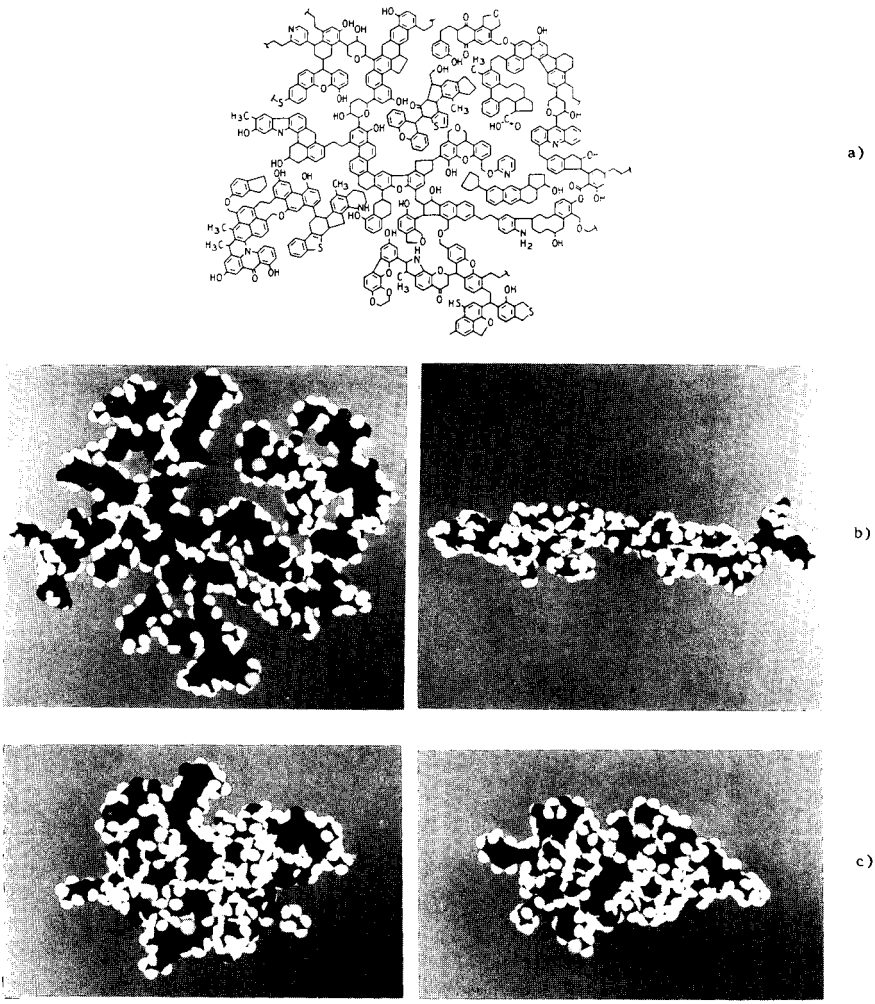

Figure 2. Shinn structure. a) Structure from literature; b) Initial CAMD-generated structure, top and side views; c) Energy-minimized CAMD structure, top and side views (same orientation, same scale).